Letters to the Editor

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MOLECULAR ORBITAL THEORY OF TRIGONALLY DISTORTED [Co, $6H_2O^{2+}$] COMPLEX

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Under an octahedral field of type O_h, $3d^7\ ^4F$ ground state of Co^{2+} ion splits up into two triplets $^4T_{1g}$, $^4T_{2g}$ and a singlet $^4A_{2g}$ of successively increasing energies. There is another term $^4P(^4T_{1g})$ arising from the same configuration $3d^7$ of the free ion, which lies about 20,000 cm^{-1} above $^4T_{1g}$ in crystals (Abragram *et al*, 1951). So that the lowest triplet state contains an admixture of ^4P through the effective orbital Lande g-factors α, α' (Bose *et al*, 1961), which are appreciably different in crystals from the value 3/2 for the free ion F-state. For trigonal distortion of the octahedron, the appropriate Hamiltonian is given by

$$H = V_{trig} + \alpha u_\zeta s_\zeta + \alpha'(u_\xi s_\xi + u_\eta s_\eta)$$

where the effect of Spin-orbit interaction takes the form $\Sigma(us)_i$ (Bose *et al*, 1960). Operating above Hamiltonian over the appropriate trigonal orbital states for the

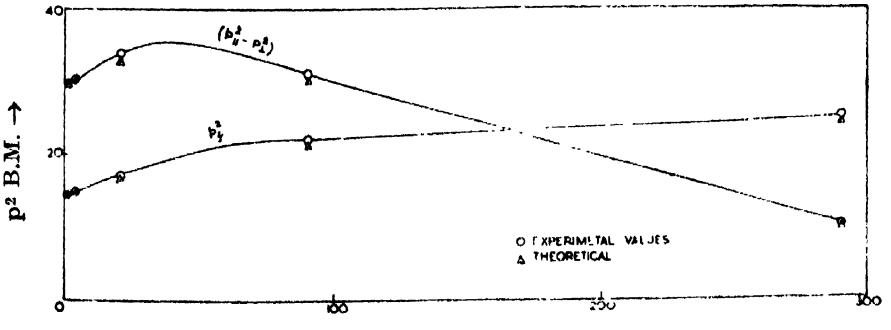

Fig. 1

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lowest triplet (Bose *et al*, 1963) formed by mixing of the central *d*- and surrounding *p*-orbitals, we get the energies and wave-functions for lowest six Kramer's doublets, ready for magnetic perturbation.

Thus we have derived a very complicated expression for the principal ionic magnetic susceptibilities $K_i (i = \| \text{ or } \perp)$ along and perpendicular to the trigonal axis of the $CoSiF_6, 6H_2O$ single crystal, which is identical for the single trigonally distorted $[Co^{2+} 6H_2O]$ complex in the unit cell sp.gr C^2_{3i} (Pauling 1930) on the basis of molecular orbital theory of Stevens (1953), Bose *et al*, (1960) and compared our theoretical with the experimental results by one of us (L.C.J.).

We had to increase the trigonal field coefficient Δ with temperature, from a value of 830 cm^{-1} at 1.67°K to 952 cm^{-1} at 90°K and then decrease it to 560 cm^{-1} at 290.4°K; the values for the spin-orbit coupling coefficient we have to take $\zeta_{\|} = -137\ cm^{-1}$ and $\zeta_{\perp} = -130\ cm^{-1}$ instead of free ion value $-180\ cm^{-1}$; the other parameters—the effective orbital Lande factors $\alpha = 1.242$; $\alpha' = 1.495$ and orbital reduction factors $k_{\|} = .975\ k_{\perp} = .93$.

The anisotropic reduction in spin-orbit coupling coefficient is due to overlap of the Co^{2+} charge clouds with *s* and *p* ligand charge clouds. The increase in Δ below 90°K is, as observed earlier, due to thermal expansion or relaxation effects but the decrease above 90°K appears to be due to some kind of phase transition reversible in character, evidence for which is available from some of our recent measurements between 90°*K* and 300°*K* (Mazumdar *et al*). Details of the theoretical developments and experimental results will be published elsewhere.

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